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(54) Title: POLYMER SUPPORTED CATALYST FOR OLEFIN POLYMERIZATION (57) Abstract The present invention is directed to a supported metallocene catalyst useful in the polymerization of α -olefins which is obtained by tethering a metallocene catalyst component to the surface of a particulate functionalized copolymeric support material.		

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1 POLYMER SUPPORTED CATALYST FOR OLEFIN POLYMERIZATION

 The present invention relates to a supported
metallocene catalyst useful for polymerizing or
copolymerizing α -olefins. More particularly, the
5 instant invention is directed to a supported
metallocene catalyst which is prepared by tethering a
metallocene catalyst component to a functionalized
copolymeric support material. The instant invention
also relates to a process for polymerizing or
10 copolymerizing α -olefins using the supported
metallocene catalysts of the present invention.

 Traditionally, ethylene and 1-olefins have
been polymerized or copolymerized in the presence of
hydrocarbon insoluble catalyst systems which comprise
15 a transition metal component and an aluminum alkyl.
More recently, active homogeneous catalyst systems
comprising a bis(cyclopentadienyl)-transition metal
dialkyl, an aluminum alkyl, and water have been found
to be useful for the polymerization of ethylene. Such
20 catalyst systems containing a cyclopentadienyl moiety
are referred to in the art as "metallocenes".

 U. S. Patent Nos. 4,404,344; 4,522,982;
4,590,914 and 4,937,299 describe various homogeneous
metallocene catalyst systems for use in α -olefin
25 polymerization reactions. These metallocene catalyst
systems typically require the use of an aluminoxane
compound as a catalyst activator.

 An advantage of the metallocene aluminoxane
homogeneous catalyst system is the very high activity
30 obtained for ethylene polymerization. Another
significant advantage is, unlike olefin polymers

1 produced in the presence of conventional heterogeneous
Ziegler catalysts, terminal unsaturation is present in
polymers produced in the presence of these homogeneous
catalysts. Nevertheless, the homogeneous metallocene
5 catalysts suffer from a disadvantage, that is, the
ratio of alumoxane to metallocene is high, for
example, in the order of 1,000 to 1 or greater. Such
voluminous amounts of alumoxane would require
extensive treatment of polymer product obtained in
10 order to remove the undesirable aluminum. A second
disadvantage of the homogeneous catalyst system, a
disadvantage also associated with traditional
heterogeneous Ziegler catalysts, is the multiple
delivery systems required for introducing the
15 individual catalyst components into the polymerization
reactor.

In an attempt to overcome these problems
mentioned hereinabove, supported-heterogeneous
metallocene catalyst systems have been developed.
20 Typically, the heterogeneous metallocene catalyst
system comprises supporting a metallocene catalyst
component on refractory inorganic oxide supports, such
as SiO_2 , Al_2O_3 , and MgO . These inorganic oxide
supports, which may be used in concert with an
25 organoaluminum compound, are available in a variety of
particle sizes and porosities. One such heterogeneous
catalyst system using a refractory oxide support is
described in U.S. Patent No. 5,086,025 to Chang. More
specifically, the Chang reference discloses a process
30 for preparing a supported metallocene alumoxane
catalyst for use in liquid or slurry phase

1 polymerization of α -olefins. The preparation of the
supported heterogeneous catalyst involves initially
reacting silica gel with an aluminum trialkyl solution
to form a support material for the metallocene
5 component. The metallocene component is then adsorbed
onto the surface of the support material.

Despite their usefulness, inorganic oxide
supports have several deficiencies. For example,
inorganic oxide supports must be calcined at high
10 temperatures or chemically treated with appropriate
reagents to remove physically adsorbed water from the
surface of the support. The presence of water on the
surface of inorganic oxide supports is well known in
the art as being a catalytic poison which can
15 adversely affect the catalytic activity of the
catalyst.

In addition, inorganic oxide supports have a
limited maximum pore size which also can restrict the
catalytic performance of the catalyst. Although large
20 pore size inorganic oxides are available, these
materials may be friable and the use thereof as
catalyst supports may, through attrition, lead to the
formation of unwanted fine particles.

Furthermore, it is well known in the art
25 that inorganic oxides not only adsorb water but other
commonly occurring catalyst poisons, such as oxygen.
Thus, great care in handling and preparing inorganic
oxide supported catalysts must always be exercised.

Moreover, since prior art supported
30 metallocene catalysts involve adsorption of the
metallocene onto the inorganic oxide support, a debate

~~1~~ exists as to whether the metallocene component is actually bound to the surface of the inorganic oxide support or is held in place as a contact ion pair in conjunction with the surface bound organometallic species. If the former is the case, the bound complex may have been the result of chloride or ligand abstraction, or the surface oxygen from the support may have been bound to the transition metal. If the latter is true, the possibility of active site migration, redistribution, and bimolecular deactivation becomes more reasonable during polymerization. All of these phenomena may contribute towards poor morphological control or less than optimal catalyst performance.

15 To overcome the above deficiencies that are commonly observed in inorganic supported catalysts and to provide a metallocene catalyst which maintains its basic ligand environment and oxidation state, many research groups have focused on substituting polymeric supports for inorganic oxide supports. See, for example, U. S. Patent Nos. 4,147,644; 5,206,199; and 5,346,925; European Patent Appln. Nos. 598,543; 285,443 and 295,312; and Canadian Patent Appln. No. 2,093,056.

25 Another example of supporting a metallocene catalyst component on a polymeric support is disclosed in Japanese Kokai Patent Appln. No. Hei 6-56928 (1994). The supported metallocene catalyst disclosed in this Japanese reference is prepared by reacting a ligand

30

1 leader of a transition metal component having halogen
atoms or an OR group, wherein R is a C₁-C₁₆
hydrocarbon, with an organometallic compound
containing a metal from Groups I-III of the Periodic
5 Table of Elements. Next, the polymeric support
material having a substitute group, such as a halogen
atom, an ester group, a carboxyl group or a hydroxy
group, is reacted and the ligand is chemically bonded
to the polymeric support. The transition-metal
10 compound precursor obtained above is then coordinated
to the ligand chemically bonded to the polymeric
support material.

Typically, polymeric supports employed in
the prior art are organic polymers such as
15 polyethylene, polypropylene, polystyrene, polyvinyl
alcohol, poly(styrene-divinylbenzene),
poly(methylmethacrylate) and the like.

The use of these polymeric supports provides
several advantages over similar olefin metallocene
20 polymerization catalyst components supported upon
inorganic oxides. For example, polymeric supports
usually require no dehydration prior to the use
thereof; they can be easily functionalized which
afford more opportunities to prepare tailor-made
25 catalysts; they are inert; they can be prepared with a
wide range of physical properties, via chemical and
mechanical means to intentionally give porosity,
morphology and size control to the catalyst; and they
offer a cost advantage over inorganic oxide supports.

30 Despite the advantages listed hereinabove,
prior art polymeric supports still possess certain

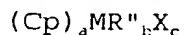
1 inherent disadvantages which decrease their
acceptability as viable replacements for inorganic
oxide supports. For instance, polymeric supports
often lack structural stability at high temperatures
5 and under some solvent conditions. Moreover, the
porosity and size of the polymeric support, due to
swelling may change drastically over the short time
duration required to prepare the catalyst.
Furthermore, the choice of the polymer support must be
10 compatible with the polymer produced in order to
insure that this incompatibility does not contribute
to the formation of gels.

It would thus be highly advantageous to
provide a polymeric support which keeps the active
15 site of the metallocene intact and which overcomes the
above drawbacks while still being useful in the
polymerization of α -olefins.

The present invention is directed to a
supported metallocene catalyst that is useful in the
20 homopolymerization or copolymerization of α -olefins
which is prepared by tethering a metallocene catalyst
component to a particulate functionalized copolymeric
support material. More particularly, the supported
metallocene catalyst of the instant invention is
25 prepared by tethering a metallocene to a particulate
functionalized copolymeric support through a bridge to
the cyclopentadienyl, indenyl or fluorenyl ring. The
particulate functionalized copolymeric supports of the
instant invention include copolymers of an α -olefin
30 and an acrylate, the latter being used in a generic
sense to include esters of acrylic as well as

1 methacrylic acid. The supported metallocene catalyst
of the instant invention, in combination with suitable
cocatalysts, provides an α -olefin polymerization
catalyst system which produces polymers comprised
5 predominantly of ethylene and/or propylene with
densities ranging from about 0.90 to about 0.97 and
having a desirable balance of rheological and physical
properties making them useful in a wide range of
applications.

10 Specifically, the present invention relates
to a supported metallocene catalyst useful for
polymerizing olefins comprising the product which is
prepared by the steps of (a) reacting a particulate
olefin copolymer support which comprises discrete
15 particles having a median particle size ranging from
about 1 up to about 1500 microns, a pore volume of
less than 0.1 cc/g and a surface area of less than
about 15 m²/g, wherein said olefin copolymer has a
melt index of from about 0.1 to about 400 and
20 containing from about 50.1 to about 99.9 weight
percent C₂, α -olefin and from about 0.1 to about 49.9
weight percent of an acrylate, with a metallated
compound containing a metal from Groups I-III of the
Periodic Table of Elements under conditions sufficient
25 to form a metallated keto-intermediate; (b) contacting
said metallated keto-intermediate of step (a) with a
transition metal compound having the formula



wherein Cp is a substituted or unsubstituted
30 cyclopentadienyl, indenyl or fluorenyl ring; M is a
metal from Group IVB, VB and VIB of the Periodic Table

1 of Elements, R^u is a hydride, a hydrocarbyl group
having from about 1 to about 20 carbon atoms, an
alkoxy group having from about 1 to about 12 carbon
atoms, a substituted or unsubstituted aryl group
5 containing from about 6 to about 12 carbon atoms, or
NR'', wherein R'' is an alkyl containing from about 1
to about 12 carbon atoms; X is a halide; a is 0 or 1;
b is 0-4; c is 0-4; and the sum of a, b, and c is
equal to the oxidation state of M; and (c) recovering
10 said contact product of step (b).

In accordance with a preferred embodiment of
the present invention, the particulate functionalized
copolymeric support is a microfine powder comprised of
particles that are spherical or substantially
15 spherical. The term "microfine" means that the
particles of the support material have a median
particle size of from about 1 to about 500 microns.
The microfine powders which are employed in the
present invention are prepared by heating a copolymer
20 to a temperature above the melting point of the
copolymer in the presence of a nonionic surfactant;
dispersing the mixture produced in the heating step in
a dispersant to produce droplets of a desired size;
and cooling the dispersion to a temperature below the
25 melting point of the copolymer.

The present invention is also directed to a
process for polymerizing one or more α -olefins. In
this process at least one α -olefin is polymerized
under olefin polymerization conditions utilizing the
30 catalyst system of the present invention which
includes the tethered metallocene as the solid

- 1 catalyst component, along with a suitable cocatalyst
component(s).

The particulate functionalized copolymeric
supports of the instant invention are copolymers of an
5 α -olefin and an acrylate. The term "acrylate" being
used in the generic sense to encompass esters of both
acrylic and methacrylic acid.

The copolymers, from which the particulate
functionalized supports of the present invention are
10 obtained, are produced by copolymerizing an α -olefin,
especially ethylene and/or propylene, with one or more
monomers selected from the group consisting of lower
alkyl acrylates, arylacrylates and methacrylate
monomers or by grafting one or more of the
15 aforementioned acrylate monomers to a polyolefin,
particularly a polypropylene or polyethylene,
backbone.

Copolymerizations of α -olefins and the above
monomers are well known and are generally carried out
20 at pressures of up to about 30,000 psi and
temperatures of from about 150°C to about 250°C in the
presence of suitable catalysts. A typical process for
copolymerizing ethylene and lower alkyl acrylates is
described in U.S. Patent No. 2,200,429, the contents
25 of which are incorporated herein by reference.

Grafting of the above acrylate monomers onto
a polyolefin backbone may be conducted by using
techniques that are well known in the art. Typical
grafting processes that may be used in the present
30 invention to graft the acrylate monomer to a
polyolefin backbone are described in U.S. Patent Nos.

1 2,987,501; 3,027,346 and 3,882,194, the contents of which are incorporated by reference.

The above-mentioned copolymers have an α -olefin as the major constituent. More preferably, the
5 copolymers of the invention have from about 50.1 to about 99.9 weight percent C_{2-3} α -olefin copolymerized with from about 0.1 to about 49.9 weight percent of the monomer. Preferably, the copolymers will contain
10 from about 70 to about 99 weight percent ethylene, propylene or mixtures thereof and from about 1 to about 30 weight percent of one of the above-identified monomers. In one highly useful embodiment, the copolymer supports comprise from about 80 to about 95
15 weight percent ethylene and about 5 to about 20 weight percent acrylate.

The acrylate monomer utilized in the present invention has the formula



where R is hydrogen or methyl and R' is an alkyl group having from about 1 to about 12 carbon atoms or an aryl group having from about 6 to about 12 carbon
25 atoms. Alkyl groups may be straight chain or branched and can be saturated or unsaturated. Aryl groups can be unsubstituted, e.g., phenyl, or can contain one or more hydrocarbyl substituents, e.g., benzyl, tolyl, xylyl.

Representative acrylate comonomers which can
30 be used for the copolymer include: methyl acrylate, ethyl acrylate, isopropyl acrylate, allyl acrylate, n-

- 1 butyl acrylate, t-butyl acrylate, neopentyl acrylate,
n-hexyl acrylate, cyclohexyl acrylate, benzyl
acrylate, phenyl acrylate, tolyl acrylate, xylyl
acrylate, 2-ethylhexyl acrylate, 2-phenylethyl
5 acrylate, n-decyl acrylate, isobornyl acrylate, n-
octadecyl acrylate, methyl methacrylate, ethyl
methacrylate, propyl methacrylate, n-butyl
methacrylate, sec-butyl methacrylate, n-pentyl
methacrylate, n-hexyl methacrylate, n-octyl
10 methacrylate, isooctyl methacrylate, isodecyl
methacrylate, lauryl methacrylate and the like.

Among the preferred acrylate comonomers,
alkyl acrylate comonomers having the above structural
formula where R is hydrogen and R' is a C₁₋₁₄ alkyl group
15 are particularly useful. Of these, methyl acrylate,
ethyl acrylate and n-butyl acrylate are especially
preferred. In a highly useful embodiment of the
invention, the particulate supports are ethylene-
methyl acrylate, ethylene-ethyl acrylate and ethylene-
20 n-butyl acrylate copolymers. An ethylene-methyl
acrylate particulate support is particularly
preferred.

The melt index of the copolymers can range
from about 0.1 up to about 400 g/10 min. or above.
25 However, in a preferred embodiment where the supports
are microfine powders comprised of particles which are
spheroidal or substantially spheroidal, the melt index
is in the range of from about 1 up to about 125, and
more preferably, from about 1 up to about 60. All
30 melt indexes referred to herein are determined at

1 190°C in accordance with ASTM D 1238, Condition E, and
are expressed in grams per 10 minutes.

5 The copolymers used to form the supported
metallocene catalysts of the invention are particulate
products comprised of discrete particles whose median
particle size can range from about 1 up to about 1500
microns, and more preferably, from about 1 to about
1000 microns. Moreover, the particulate support
material of the present invention is further
10 characterized as having a pore volume of less than
about 0.1 cc/g and a surface area which is less than
about 15m²/g.

The copolymer powders can be obtained by
spray drying or the copolymer can be precipitated from
15 solution by the addition of a suitable precipitating
agent, e.g., methanol. The particulate supports
obtained by spray drying the copolymer or copolymers
may also be ground or milled to produce powders within
the acceptable size range. Mechanical grinding may be
20 carried out under ambient conditions if the copolymer
has a sufficiently high melting point and does not
degrade under the grinding conditions; however, it is
more customary to cryogenically grind the copolymers.
After grinding, the powders can be sieved to recover
25 particles of the desired size and particle size
distribution. Suitable particulate supports can also
be produced using other conventional solution and
dispersion processes.

In a particularly useful embodiment of the
30 invention, the supports are "microfine" powders of
functionalized copolymers obtained by dispersion

1 processes. Particles produced by these processes are
spheroidal or substantially spheroidal in shape.
Microfine powders produced using dispersion processes,
in addition to being spheroidally shaped particles,
5 also have substantially narrower particle size
distributions than reactor powders or powders produced
by precipitation, grinding or milling.

Preferred microfine functionalized
copolymeric supports are comprised of discrete
10 particles which are spheroidally or substantially
spheroidally shaped and have a median particle size
(diameter) of from about 1 micron to about 500
microns. More preferably, the median particle size is
from about 5 microns to about 300 microns and in an
15 especially useful embodiment the median particle size
is from about 20 to about 200 microns. Median
diameters as used herein are obtained from the
particle volume distribution curve.

The copolymers of the present invention are
20 converted to microfine powders using the dispersion
technique of U.S. Patent Nos. 3,422,049, 3,432,483 and
3,746,681, details of which are incorporated herein by
reference. In the powder-forming operation, the
copolymer is charged to the reactor with a polar
25 liquid medium and nonionic surfactant and a dispersion
is formed in accordance with conventional dispersing
procedures described in the art. The dispersing
apparatus may be any device capable of delivering
sufficient shearing action to the mixture at elevated
30 temperature and pressure. Conventional propeller
stirrers designed to impart high shear can be used for

1 ~~this purpose.~~ The vessel may also be equipped with
baffles to assist in dispersing the copolymer.
Particle size and particle size distribution will vary
depending on the shearing action which, in turn, is
5 related to the stirrer design and rate of stirring.
Agitation rates can vary over wide limits but the
speed of the stirrer will usually be controlled so
that the tip speed is between about 400 and about 4000
ft/min and, more commonly, about 800 and about 3500
10 ft/min. Higher tip speeds are generally used for
batch operation, usually about 2500-3500 ft/min. Tip
speeds for continuous procedures most generally range
between about 800 and about 3000 ft/min.

The dispersion process is typically carried
15 out in a vessel which enables the powder-forming
process to be conducted at elevated temperature and
pressure. In the usual batch process, all of the
ingredients are charged to the vessel and the mixture
is heated to a temperature above the melt point of the
20 copolymer. While the temperature will vary depending
on the specific polymer being used, it will typically
range from about 175°C to about 250°C. Since the
fluidity of polymers is temperature related, it may be
desirable to carry out the process at temperatures
25 substantially above the melt point of the copolymer to
facilitate formation of the dispersion; however, the
temperature should not exceed the thermal degradation
temperature of the polymer.

Stirring is commenced after the desired
30 temperature is reached and continued until a
dispersion of the desired droplet size is produced.

- 1 This will vary depending on the particular copolymer
being used, temperature, amount and type of
surfactant, and other process variables, but generally
will range from about 5 minutes to about 2 hours.
- 5 Stirring is most commonly maintained for a period of
from about 10 to about 30 minutes.

A polar liquid medium which is not a solvent
for the copolymer is employed as the dispersant in the
formation of the microfine powder support. These
10 polar media are hydroxylic compounds and can include
water, alcohols, polyols and mixtures thereof. The
weight ratio of polar liquid medium to polymer ranges
from about 0.8:1 to about 9:1 and, more preferably,
from about 1:1 to about 5:1. It is particularly
15 advantageous to use water as the dispersing medium or
a liquid medium where water is the major component.

The pressure of the process is not critical
so long as a liquid phase is maintained. In general,
the pressure can range from about 1 up to about 250
20 atmospheres. The process can be conducted at
autogenous pressure or the pressure can be adjusted to
exceed the vapor pressure of the liquid medium at the
operating temperature. Most generally, with aqueous
dispersions, the pressure will range from about 5 to
25 about 120 atmospheres.

To form acceptable dispersions, one or more
dispersing agents are necessarily employed. Useful
dispersing agents are nonionic surfactants which are
block copolymers of ethylene oxide and propylene
30 oxide. Preferably, these nonionic surfactants are
water-soluble block copolymers of ethylene oxide and

1 propylene oxide and have molecular weights greater
than about 3500. Most will contain a major portion by
weight of ethylene oxide and are obtained by
polymerizing ethylene oxide onto preformed
5 polyoxypropylene segments. The amount of nonionic
surfactant employed can range from about 4 to about 50
percent, based on the weight of the copolymer. Most
preferably, the nonionic surfactant is present in a
concentration of from about 7 to about 45 percent,
10 based on the weight of the copolymer.

Useful nonionic surface active agents of the
above type are manufactured and sold by BASF
Corporation, Chemicals Division under the trademark
Pluronic. These products are obtained by polymerizing
15 ethylene oxide onto the ends of a preformed
polyoxypropylyc base. Both the molecular weight of
the polyoxypropylene base and the polyoxyethylene
segments can be varied to yield a wide variety of
products. One such compound found to be suitable in
20 the practice of the process of this invention is the
product designated as F-98 wherein a polyoxypropylene
of average molecular weight of 2,700 is polymerized
with ethylene oxide to give a product of molecular
weight averaging about 13,500. This product contains
25 20 weight percent propylene oxide and 80 weight
percent ethylene oxide. Other effective Pluronic®
surfactants include F-88 (M.W. 11,250, 20% propylene
oxide, 80% ethylene oxide), F-108 (M.W. 16,250, 20%
propylene oxide, 80% ethylene oxide), and P-85 (M.W.
30 4,500, 50% propylene oxide, 50% ethylene oxide).
These compounds, all containing at least about 50

1 weight percent ethylene oxide and having molecular
weights of at least 4,500, are highly effective as
dispersing agents for the aforementioned copolymers.

It is also possible to employ products sold
5 under the trademark Tetronic which are prepared by
building propylene oxide block copolymer chains onto
an ethylenediamine nucleus and then polymerizing with
ethylene oxide. Tetronic[®] 707 and Tetronic[®] 908 are
most effective for the present purposes. Tetronic[®]
10 707 has a 30 weight percent polyoxypropylene portion
of 2,700 molecular weight polymerized with a 70 weight
percent oxyethylene portion to give an overall
molecular weight of 12,000. Tetronic[®] 908, on the
other hand, has a 20 weight percent polyoxypropylene
15 portion of 2,900 molecular weight polymerized with an
80 weight percent oxyethylene portion to give an
overall molecular weight of 27,000. In general,
useful Tetronic[®] surfactants have molecular weights
above 10,000 and contain a major portion by weight of
20 ethylene oxide.

The powder-forming process may also be
conducted in a continuous manner. If continuous
operation is employed, the ingredients are
continuously introduced to the system while removing
25 the dispersion from another part of the system. The
ingredients may be separately charged or may be
combined for introduction to the autoclave.

The particulate copolymer supports and
especially the microfine spheroidal powders described
30 hereinabove are then used to prepare the supported
metallocene catalysts of the instant invention.

1 In accordance with the present invention,
the particulate copolymer is reacted with a metallated
compound under conditions sufficient to form a
metallated keto intermediate and an associate alcohol.

5 The metallated compounds employed in the
present invention are well known to those skilled in
the art and they include substituted or unsubstituted
cyclopentadienylide, indenylide or fluorenylide
compounds which contain a metal from Groups I-III of
10 the Periodic Table of Elements. Illustrated examples
of such compounds include, but are not limited to,
sodium cyclopentadienylide, lithium
cyclopentadienylide, potassium cyclopentadienylide,
cyclopentadienylthallium, sodium pentamethyl
15 cyclopentadienylide, lithium pentamethyl
cyclopentadienylide, bis-(cyclopentadienyl) magnesium,
bis-(cyclopentadienyl) calcium, sodium indenylide,
lithium indenylide, sodium fluorenylide, lithium
fluorenylide and the like. Of these metallated
20 compounds, the cyclopentadienylide compounds are
particularly preferred. Sodium cyclopentadienylide is
the most preferred metallated compound employed in the
present invention.

Typically in the present invention, from
25 about 0.001 to about 10 mmol of metallized compound
per gram of particulate copolymeric support is
employed. This may mean that there is an excess
amount of a metallated compound present relative to
the amount of functional groups present on the
30 copolymeric support. The maximum amount of metallated
compound is determined by the number of functional

1 groups present on the copolymer support. More preferably, from about 0.01 to about 2 mmol metallated compound per gram of particulate support is employed in foregoing reaction step.

5 The above reaction of the particulate copolymer support and the metallated compound is carried out in an inert atmosphere, such as N₂ or Ar, and in the presence of an ether solvent such as tetrahydrofuran (THF), dimethyl ether, diethyl ether,
10 di-n-propyl ether, diisopropyl ether, di-n-butyl ether, divinyl ether, diallyl ether, diphenyl ether, 1,4-dioxane, dimethoxyethane and the like. In a preferred embodiment of the present invention, the foregoing reaction is carried out in a N₂ atmosphere,
15 and THF is used as the solvent. Solvents such as toluene, benzene and xylene are also contemplated in the present invention.

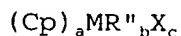
The aforementioned reaction of the particulate copolymer support and the metallated
20 compound is conducted at a temperature of from about 0° to about 100°C for a period of time from about one hour to about five days. More preferably, the above reaction is conducted at a temperature of from about 15° to about 75°C for a period of time from about one
25 day to about four days. Most preferably, the above reaction which results in the formation of the metallated keto- intermediate is conducted at a temperature of from about 20°C to about 30°C for up to about three days.

30 All or a portion of the solvent may be removed after this reaction and the intermediate

1 product produced may be washed, if desired. While it
is not necessary, it is possible to wash and/or dry
the intermediate product before contacting with the
transition metal compound. Polymeric resins of high
5 bulk density may be produced using catalysts which
have been prepared without washing between contacting
steps. If all or part of the solvent is removed from
the intermediate product, it will be redispersed in
fresh solvent prior to contacting with the transition
10 metal compound.

The metallated keto intermediate is then
contacted with a transition metal compound under
conditions sufficient to bind the transition metal to
the cyclopentadienyl, indenyl or fluorenyl ring which
15 is bound through the keto-bridge to the particulate
copolymer support material. This reaction provides
the tethered metallocene solid catalyst composition of
the instant invention.

Suitable transition metal compounds that are
20 employed in the present invention are represent by
general formula



wherein Cp is a substituted or unsubstituted
cyclopentadienyl, indenyl or fluorenyl ring; M is a
25 metal from Group IVB, VB or VIB of the Periodic Table
of Elements; Rⁿ is a hydride, a hydrocarbyl group
having from about 1 to about 20 carbon atoms, an
alkoxy group having from about 1 to about 12 carbon
atoms, a substituted or unsubstituted aryl group
30 containing from about 6 to about 12 carbon atoms, or
NR^{n'}, wherein R^{n'} is an alkyl containing from about 1

1 to about 12 carbon atoms; X is a halide; a is a 0 or
1; b is 0-4; c is 0-4; and the sum of a, b and c is
equal to the oxidation state of M.

Exemplary hydrocarbyl radicals are methyl,
5 ethyl, propyl, butyl, acyl, isoamyl, hexyl, isobutyl,
heptyl, octyl, nonyl, decyl, cetyl, 2-ethylhexyl,
phenyl and the like.

Exemplary alkoxys are methoxy, ethoxy,
propoxy, butoxy and the like. Of these, methoxy is
10 most particularly preferred.

Exemplary halides include chloride, bromide,
fluoride and iodide. Of these, chloride is most
particularly preferred.

Suitable transition metal compounds that
15 encompass the above formula include, but are not
limited to, titanium trichloride, titanium
tetrachloride, zirconium tetrachloride, hafnium
tetrachloride, (cyclopentadienyl)titanium trichloride,
(cyclopentadienyl)zirconium trichloride,
20 (cyclopentadienyl)hafnium trichloride, zirconium
tetramethyl, zirconium tetramethoxy, zirconium
tetraethoxy, titanium tetramethyl, titanium
tetramethoxy, titanium tetraethoxy,
(cyclopentadienyl)zirconium tribromide,
25 (cyclopentadienyl)zirconium trimethyl,
(cyclopentadienyl)zirconium triphenyl,
(cyclopentadienyl)zirconium trimethoxy, zirconium
tetra((dimethyl)amide), zirconium
tetra((diethyl)amide), cyclopentadienyl zirconium
30 dimethylamide dichloride and the like.

1 ~~Of these transition metal compounds,~~
zirconium compounds are particularly preferred. The
most preferred zirconium compounds are zirconium
5 tetrachloride and cyclopentadienyl zirconium
trichloride. It should be noted that the transition
metal compounds may be associated with a suitable
solvent. An example of such a compound is $\text{ZrCl}_4(\text{THF})_2$
where tetrahydrofuran is utilized as the solvent.

10 The above reaction is carried out in the
presence of a solvent mentioned hereinabove under an
inert gas atmosphere. Moreover, the reaction is
conducted at a temperature of from about 0°C to about
 100°C for a period of time up to about five days.
More preferably, the reaction of the intermediate
15 compound and the transition metal compound is carried
out at a temperature of from about 15°C to about 75°C
for a period of about 30 minutes to about two days.
Most preferably, the reaction is conducted at a
temperature of from about 20°C to about 30°C for a
20 period of time up to about 24 hours.

While it is not necessary, the supported
metallocene catalyst of the present invention may be
washed and dried after recovery. After the transition
metal is reacted with the intermediate compound, the
25 supported metallocene catalyst is recovered using
conventional procedures, such as decantation and
centrifugation, and is ready for use in
polymerizations.

Supported metallocene catalysts obtained in
30 this manner are fine, free-flowing powders having
particles not differing substantially in size, shape

1 and particle size distribution from that of the
copolymer support material used for their preparation.
The supported metallocene catalysts of the instant
invention contain from about 0.01 up to about 10
5 weight percent transition metal based on the total
weight of said supported catalyst. More typically,
transition metal contents will range from about 0.1 to
about 2.0. The supported metallocene catalysts of
this invention are generally employed with a
10 cocatalyst, sometimes also referred to as a catalyst
promoter or catalyst activator. The cocatalyst
employed in the present invention contains at least
one metal selected from Groups IA, IIA, IIB, IIIB, and
IVB of the Periodic Table of Elements. Such
15 cocatalysts are known and widely used in the
polymerization art and can include metal alkyls, metal
hydrides, metal alkylhydrides, and metal alkylhalides,
such as alkyllithium compounds, dialkylzinc compounds,
trialkylboron compounds, trialkylaluminum compounds,
20 alkylaluminum halides, alkylaluminum hydrides, and the
like. Mixtures of cocatalytic agents can also be
employed. Illustrative organometallic compounds which
can be used as cocatalyst include n-butyllithium,
diethylzinc, di-n-propylzinc, triethylboron,
25 trimethylaluminum, triethylaluminum,
triisobutylaluminum, tri-n-hexylaluminum,
ethylaluminum dichloride, ethylaluminum dibromide,
ethylaluminum dihydride, diethylaluminum chloride, di-
n-propylaluminum chloride, and the like. Linear or
30 cyclic aluminoxanes, which are preferred, such as
those described in U. S. Patent Nos. 4,897,455 to

1 Wellborn, Jr. and 4,912,075 to Chang and dimeric
compounds of the formula $(Y)_2-Al-O-Al-(Y)_2$ where each Y
is the same or different and is an alkyl containing
from about 1 to about 6, preferably from about 2 to
5 about 4, carbon atoms can also be used as the
cocatalyst. Preferred cocatalysts are the linear or
cyclic aluminoxanes and the dimeric aluminum compounds
described above. Methylaluminoxanes (MAO) are highly
useful cocatalysts for the supported metallocene
10 catalysts of the invention and is particularly
preferred.

Cocatalysts are employed in amounts
effective to promote (increase) the polymerization
activity of the supported metallocene catalyst. The
15 amount of cocatalyst used can vary widely but most
generally the molar ratio of the metal of the
cocatalyst, based on the transition metal compound,
ranges from about 1:1 to about 10,000:1 and, more
preferably, from about 50:1 to about 5,000:1. The
20 catalyst may be activated in-situ by adding the
cocatalyst and supported catalyst separately to the
polymerization or the supported catalyst and activator
may be pre-contacted before introduction to the
polymerization reactor.

25 Cocatalysts for polymerization may be
employed singly in the manner described, or in concert
with other such modifiers, activators or promoters to
enhance activity or influence resin properties. The
use of cocatalyst modifiers is described, e.g. in U.S.
30 Patent No. 5,334,567 to Menon et al. regarding
halosilanes; U.S. Patent Nos. 4,559,318 to Smith et

- 1 al., 4,866,021 to Miro et al., 5,006,618 to Miro et
al. regarding halocarbons; U.S. Patent No. 4,250,287
to Matlack regarding aromatic esters; U.S. Patent Nos.
3,786,032 to Jennings et al. and 4,611,038 to Brun et
5 al. regarding additional organometallic activators,
and U.S. Patent No. 5,275,991 to Buehler et al.
regarding alkoxysilanes.

- Preferred compounds which may be employed as
cocatalyst modifiers include halocarbons such as
10 carbon tetrachloride, carbon tetrabromide,
dichloromethane, dibromomethane, 1,1,1-trichloroethane
and a number of commonly available chlorofluorocarbons
(CFC's) and hydro-chlorofluorocarbons (HCFC's);
halosilanes such as silicon tetrachloride,
15 trichlorosilane, dichlorosilane; and alkoxysilanes
such as dimethoxysilane, diethoxysilane,
diisopropoxysilane, trimethoxysilane and
tetramethoxysilane.

- A highly preferred class of cocatalyst
20 modifiers that may be used in the present invention
are the phenylborate salts. This class of cocatalyst
modifier is well known to those skilled in this art.
Suitable examples of such modifiers include, but are
not limited to, triethylammonium tetraphenylborate,
25 tri(n-butyl)ammonium tetraphenylborate,
trimethylammonium tetraphenylborate,
dimethyldiphenylammonium tetraphenylborate,
methylpyridinium tetraphenylborate, benzylpyridinium
tetraphenylborate, trimethylsulfonium
30 tetraphenylborate, triethylammonium
tetrakis(pentafluorophenyl) borate, triphenylammonium

1. tetrakis(pentafluorophenyl) borate, methyldiphenylammonium tetrakis(pentafluorophenyl) borate, anilinium tetrakis(pentafluorophenyl) borate, methylanilinium tetrakis(pentafluorophenyl) borate, 5 dimethyl(m-nitroanilinium tetrakis(pentafluorophenyl) borate, pyridinium tetrakis(pentafluorophenyl) borate, N-methylpyridinium tetrakis(pentafluorophenyl) borate, trimethylsulfonium tetrakis(pentafluorophenyl) borate, tetraphenylphosphonium tetrakis(pentafluorophenyl) 10 borate, triphenylphosphonium tetrakis(pentafluorophenyl) borate, hexafluoroarsenic acid triethylammonium and the like.

The catalyst of the invention can be used in virtually any polymerization procedure where supported 15 metallocene catalysts have heretofore been utilized. This includes both gas phase (stirred or fluidized bed) polymerizations and solution polymerizations. They are highly effective for stirred bed and fluidized bed polymerization processes which are 20 carried out in the substantial absence of a liquid reaction medium. Such procedures are well known and described in the prior art and may be conducted in a single reactor or in multiple reactors connected in series. The catalysts are equally effective for use 25 in particle form (slurry) processes which are also described in the prior art. These polymerizations are carried out in a liquid organic medium in which the catalyst is suspended. A pressure sufficient to maintain the organic diluent and at least a portion of 30 the monomer in the liquid phase is maintained.

1 The supported metallocene catalysts of the
invention are useful for the preparation of
homopolymers and copolymers of alpha-olefins
containing from about 2 to about 8 carbon atoms. Most
5 preferably, they are used to produce polymers
comprised predominantly of ethylene and/or propylene
with densities ranging from about 0.90 to about 0.97
and having a desirable balance of rheological and
physical properties making such polymers useful in
10 applications such as blow molding, injection molding,
rotomolding, rotolining, extrusion, coextrusion, film
forming and the like.

 Moreover, the polymers produced herein have
the same morphology as the supported catalyst used in
15 the polymerization process. That is, the polymers
produced by the instant process have substantially
spherical particles and a median particle size which
depends on both the median particle size of the
catalyst particles and the amount of polymer produced
20 per unit amount of catalyst employed in the
polymerization. The median particle size can thus
range from about 10 to about 5000 microns.
Prepolymerization methods may be used to further
improve upon the particle size of the polymer
25 produced. Such prepolymerization methods are well
known to those skilled in the art. Furthermore, the
polymer particles produced in the present invention
are compatible with the functionalized copolymeric
supports. Thus, no residual gels are formed during
30 the polymerization process which are attributable to
the catalyst support.

1 The following examples are given to
illustrate the scope of the invention. As will be
apparent to those skilled in the art, numerous
variations are possible and thus the scope of this
5 invention should not be limited thereto.

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1 PREPARATION OF PARTICULATE SUPPORTS

 An electrically heated two-liter Parr
 [trademark] pressure autoclave equipped with a
5 thermowell and thermocouple connected to a digital
display was used to prepare an ethylene-methyl
acrylate copolymer (EMA) microfine powder support
following the general procedure set forth in the U.S.
Patent No. 3,422,049, the contents of which are
10 incorporated herein by reference. The autoclave was
equipped with an agitator and a Strahman [trademark]
valve to permit rapid discharge of the hot polymer
dispersion into a 5 gallon stainless steel discharge
tank which was connected to the reactor via a 1"
15 diameter stainless steel line. The hot dispersion was
rapidly discharged into this tank containing
approximately 6.5 liters of 20-23°C water at the
completion of each run. The hot dispersion was
introduced below the surface of the water. The
20 autoclave agitator used had three, six-bladed,
impellers and was driven by a 2 HP DC variable speed
motor.

 The powder produced in this operation was
analyzed using laser light scattering to measure the
25 size distribution thereof by volume. This technique
used the principle of diffraction of the particles as
the measurement means. A Model 2600C Malvern Particle
Size Analyzer with proper lens configuration for the
expected particle size interfaced with a computer was
30 used. It read the diffraction pattern and digitally
performed the necessary integrations. For the powder

1 analysis, water was charged to the water bath and
circulated through the sample measuring chamber.
After obtaining the baseline measurement, the agitator
and sonic vibrator were activated and the copolymer
5 powder was added to the water bath until the
obscuration reading was 0.3. Mixing and circulation
were controlled to obtain acceptable dispersion
without excessive foaming. A drop of liquid detergent
was added to facilitate dispersion. After eight
10 minutes agitation, measurements were commenced and the
size distribution data was automatically tabulated.
The cumulative volume undersize and volume frequency
was tabulated for 32 size classes together with useful
derived parameters. A logarithmic plot was also
15 produced. Duplicate runs were made for each copolymer
powder sample. The particle size reported in the
examples was the median diameter $D(v,0.5)$ for the
volume distribution curve. The range reported in the
examples was for 80 percent of the volume distribution
20 curve, i.e., from $D(v,0.1)$ to $D(v,0.9)$. In other
words, ten percent of the powder particles were sized
below the recited lower limit and 10 percent of the
powder particles were larger than the upper recited
particle size limit. This range provides a
25 convenient means of comparing powders.

Following the procedure of Example I of U.
S. Patent No. 3,422,049, a particulate microfine
support was produced from an ethylene-methyl acrylate
copolymer containing 16.5 wt.% methyl acrylate having
30 a density of 0.939, a melt index of 6.0, a melting
point, as determined by Differential Scanning

1 Colorimetry using the procedures of ASTM Test
Procedures D-3417 and D-3418, of 86°C, and a VICAT
Softening Point, as determined by ASTM Test Procedure
D-155, Condition B, of 57°C.

5 In the above powder preparation, 450 grams
of the copolymer was combined with 180 grams
dispersing agent (Pluronic F-98) and 810 grams water.
The reactor was sealed, heated and when the
temperature reached about 210°C agitation (about 3200-
10 3340 rpm)
was commenced.

The powder thus prepared had a median
particle size, $D(v,0,5)$ of about 32.4 microns and a
particle size range (in microns for 80% of the volume
15 distribution curve) of about 14.3 - 61.6 microns.
Furthermore, the EMA support prepared from the above
procedure was a free-flowing powder comprised of
discrete particles having spherical morphology, i.e.,
the individual particles were spherical or
20 substantially spherical in shape.

The EMA copolymer support used in the
following examples was also more fully characterized
and was found to have a surface area of about 2.1
 m^2/g , a pore volume of 0.021 cc/g and an average pore
25 radius of 203 Å as determined by the Brunauer, Emmett,
Teller (BET) method. These measurements were carried
out using an AUTOSORB-6 [trademark] instrument and the
physical measurements were determined using techniques
described in S. Lowell et al., "Powder Surface Area and
30 Porosity", 2nd Ed., Chapman and Hall, London, 1984.
Furthermore, the copolymer support had a weight

1 average molecular weight (M_w) of 110,400, number
average molecular weight (M_n) of 24,700 and MWD (M_w/M_n)
of 4.50.

5 Additionally, a particulate support was
obtained by cryogenically grinding EMA. Cryogenic
grinding of this sample was conducted by mechanical
means, using a Wiley mill which was equipped with a
recirculating refrigerant. The polymer sample, i.e.
EMA, was ground along with dry ice so as to not incur
10 polymer melting. The polymer was also ground so as to
pass through a 20 mesh screen size. The resulting
ground powder has an average particle size of about
590 microns and a particle size distribution of about
297 to about 840 microns.

15 The microfine EMA copolymer support and the
cryogenic ground support were employed in the
preparation of the supported tethered metallocene
catalysts in the examples which follow.

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1 PREPARATION OF SUPPORTED TETHERED METALLOCENE
 CATALYSTS AND POLYMERIZATIONS

5 Example I:

 To illustrate the preparation of a supported
metallocene catalyst of the instant invention, five
(5.0) grams of the ground EMA support material
prepared above was slurried with 75 ml dry THF under a
10 nitrogen atmosphere in a 250 ml round-bottom Schlenk
flask equipped with a stirring bar. One (1.0) ml of
2.0M sodium cyclopentadienylide (NaCp) in THF (2.0
mmol) was added via syringe to the slurry under N₂ at
room temperature. The above reaction proceeded for
15 about 72 hours, at which time a purple-red color was
noted on the EMA support. Without wishing to be bound
by any theory, this purple-red color is believed to be
attributed to the electron-delocalized complex, i.e.
the intermediate, formed upon bonding to the EMA.

20 To illustrate that a complex was formed on
the EMA support, the intermediate was analyzed using a
Nicole 60SXR FTIR. Upon spectral subtraction of the
EMA support, a small peak at 1650 cm⁻¹ corresponding to
a carbonyl stretch was identified. This stretch was
25 in agreement with values reported in the literature
for related keto-cyclopentadienides, and thus
suggested that a unique carbonyl species, i.e. a keto-
cyclopentadienide intermediate, had been formed on the
polymer backbone. The intermediate
30 ("EMA/NaCp"), was isolated, washed free of excess NaCp

1 with heptane, and then dried in vacuo. The dried
intermediate was then reslurried in fresh THF.

5 A THF solution of $\text{ZrCl}_4(\text{THF})_2$ (0.377g;
0.999 mmol) was added via cannula at a target loading
of about 0.2 mmol Zr/g EMA. The reaction proceeded
for about two hours after which the product was
filtered and washed with fresh THF (100 ml) to remove
any unreacted ZrCl_4 and possibly any unbound Cp_2ZrCl_2 .
10 The washed product was then dried in vacuo to give a
metallocene catalyst supported through one or both of
its cyclopentadienyl rings.

Analysis of the metallocene catalyst
revealed that the catalyst contained 0.56% Zr (0.06
15 mmol Zr/g EMA).

The catalyst was used to prepare ethylene
homopolymers. The polymerization was conducted in a
one liter autoclave reactor which was charged with 500
ml dried, deoxygenated isobutane. Hydrogen was added
20 to control the molecular weight and a modified
methylaluminoxane, obtained from Texas Alkyls as a
2.24M Al concentrated solution in heptane (MMAO-3A),
was used as the cocatalyst. The details of the
polymerization conditions as well as the
25 characteristics of the resins produced are provided in
Table 1.

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1 **EXAMPLE II:**

 A supported metallocene catalyst containing the ground EMA support of Example I was prepared as follows:

5 4.06 grams of ground EMA was placed in a 250 ml roundbottom Schlenk flask equipped with a stirbar and was thereafter slurried with 50 ml of dry THF. One (1.00) ml of 2.0M NaCp in THF (2.0 mmol) was added via syringe to the slurried EMA while under nitrogen
10 and at room temperature and the reaction was allowed to proceed with stirring for 72 hours. Over the course of the reaction time, the solution and ultimately the polymer took on a purple color. Once the reaction was completed, the THF was removed in
15 vacuo to the point where the polymer was clumpy, but had excess THF. Approximately 200 ml of heptane was then added, the slurry was stirred briefly, then settled. A brackish brown supernatant was decanted off via cannula and discarded. The treated polymer
20 was washed a second time with 200 ml heptane and decanted. A golden brown material remained which was dried in vacuo.

 The remaining golden brown material was slurried once again in THF, then a solution of 0.105 g
25 CpZrCl₃ (0.4 mmol) in 50 ml THF was added to the slurry. In the first 10 minutes, after addition, both the polymer and the solution changed to a wheaten yellow color. The reaction was concentrated down to approximately 25 ml THF and then was stirred overnight
30 at room temperature. The THF was filtered off, then the remaining catalyst was washed twice with 30 ml of

1 ~~heptane and dried in vacuo to give a metallocene~~
catalyst supported through a bridge to only one
cyclopentadienyl ring. 2.7 Grams of a light caramel
colored powder was recovered. Analysis revealed that
5 the catalyst contained 0.53% Zr (0.058 mmolZr/g).

The catalyst was used to polymerize
ethylene. The details of the polymerization in
isobutane are provided in Table 1 whereas the
polymerization data in toluene are tabulated in Table
10 2.

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1 EXAMPLE III:

 A supported metallocene catalyst containing the aforementioned particulate microfine EMA copolymer support was prepared and used for the polymerization
5 of ethylene in this example. Specifically, the supported metallocene catalyst was prepared as follows:

 5.2 grams of the particulate microfine EMA support, was placed in a 250 ml roundbottom Schlenk
10 flask equipped with an egg-shaped stirbar and was slurried with 75 ml of dry THF. Two (2.00) ml of 2.0M NaCp in THF (4.0 mmol) was added via syringe to the slurried EMA, while under nitrogen and at room temperature, and the reaction was allowed to proceed
15 with stirring for 4 days. Over the course of the reaction the solution and ultimately the polymer took on a caramel color. Once complete, the THF was filtered without prior reduction of volume. The polymer was washed once with heptane, filtered, then
20 dried in vacuo to produce a grayish-purple powder.

 The dried intermediate was again slurried in a 20 ml of THF, then a solution of 0.153 grams CpZrCl₄ (0.582 mmol) in 30 ml of THF was added to the slurry. Upon addition of the solution, the polymer reverted to
25 a caramel color. The reaction was stirred overnight at room temperature, then was filtered. The powder was washed twice with heptane and dried in vacuo. 4.53 Grams of a light purple-grey powder was recovered.

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1 The resulting catalyst contained 0.44% Zr
(0.048 mmol Zr/g). The polymerization details are
tabulated in Table 1.

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1 EXAMPLE IV:

 A supported metallocene catalyst containing the particulate microfine EMA support material was prepared as follows:

5 5.0 grams of particulate microfine EMA support was placed in a 250 ml roundbottom Schlenk flask equipped with stirbar and was slurried with 75 ml of dry THF. 4.50 ml of 2.0M NaCp in THF (9.0 mmol) was added via syringe to the slurried EMA while under
10 nitrogen and at room temperature. The reaction was allowed to proceed with stirring for 4 days. Over the course of the reaction, the solution and ultimately the polymer took on a purple color. After the 4 days, THF was removed in vacuo. The polymer was washed with
15 50 ml of fresh THF and filtered, leaving a grayish-purple powder.

 The dried intermediate was again slurried in 50 ml of THF, then a solution of 1.0 grams $\text{ZrCl}_4(\text{thf})_2$ (2.65 mmol) in 50 ml of THF was added to the slurry.
20 Upon addition of the solution, the polymer changed to a flaxen-yellow color. The reaction was stirred for one hour at room temperature, then the THF was filtered off, leaving a grayish polymer powder. The filtrate, which had a yellowish tint, was discarded.
25 The powder was washed once with heptane, then filtered and dried in vacuo. 4.80 Grams of a light purple-grey powder were recovered.

 The catalyst contained 0.72% Zr (0.079 mmol Zr/g).

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1 Table 1: Slurry Polymerization Results
with Isobutane

	I	I	II	III
5 Catalyst wt. (g)	0.33	0.34	0.15	0.36
H ₂ (mmol)	4	4	4	4
Rx Temp. (°C)	90	70	70	90
Rx Pressure (psig)	550	500	450	500
10 Al/Zr	2200	2100	6400	1300
Time (min)	60	60	30	60
Activity (g/g cat·hr)	479	360	1196	171
MI ¹	1.26	0.32	0.239	1.11
15 MIR ²	24.3	27.9	30.46	33.2
MW ³	70,700	110,200	105,200	190,790
MWD ⁴	2.4	2.7	3.0	5.6

20 ¹ Determined by ASTM D-1238, Condition E, reported as g/10 minutes.

² Determined by flotation in a density gradient column after annealing an extrudate sample for 30 minutes at 100°C to approach equilibrium crystallinity.

25 ³ Weight average molecular weight determination was made using a Waters GPC on a mixed sized, crosslinked divinylbenzene column with 1,2,4-trichlorobenzene as a solvent at 135°C with a refractive index detector.

⁴ The ratio of Mw vs Mn, i.e., MWD, was also determined by GPC.

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1 Table 2: Slurry Polymerization Results
 in Toluene

		II	II	II
5	Catalyst wt. (g)	0.18	0.17	0.16
	H ₂ (mmol)	4	4	4
	Rx Temp. (°C)	70	70	90
	Rx Pressure (psig)	200	400	200
10	Al/Zr	5333	2259	2400
	Time (min)	60	60	60
	Activity (g/g cat·hr)	1092	653	679
	MI ¹	1.91	0.73	23.86
15	MIR ²	18.9	17.8	NA
	MW ³	85,800	128,800	50,600
	MWD ⁴	2.4	2.3	1.8

20 Determined by ASTM D-1238, Condition E, reported
as q/10 minutes.

2. Determined by flotation in a density gradient column after annealing an extrudate sample for 30 minutes at 100°C to approach equilibrium crystallinity.

25 Weight average molecular weight determination was made using a Waters GPC on a mixed sized, crosslinked divinylbenzene column with 1,2,4-trichlorobenzene as a solvent at 135°C with a refractive index detector.

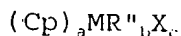
30 ⁴ The ratio of Mw vs Mn, i.e., MWD, was also determined by GPC.

1. What is claimed is:

1. A supported metallocene catalyst useful for polymerizing olefins comprising the product which is prepared by the steps of:

(a) reacting a particulate olefin copolymer support which comprises discrete particles having a median particle size ranging from about 1 up to about 1500 microns, a pore volume of less than 0.1 cc/g and a surface area of less than about 15 m²/g, wherein said olefin copolymer has a melt index of from about 0.1 to about 400 and containing from about 50.1 to about 99.9 weight percent C₂, α-olefin and from about 0.1 to about 49.9 weight percent of an acrylate, with a metallated compound containing a metal from Groups I-III of the Periodic Table of Elements under conditions sufficient to form a metallated keto-intermediate;

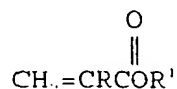
(b) contacting said metallated keto-intermediate of step (a) with a transition metal compound having the formula



wherein Cp is a substituted or unsubstituted cyclopentadienyl, indenyl or fluorenyl ring; M is a metal from Group IVB, VB and VIB of the Periodic Table of Elements; R'' is a hydride, a hydrocarbyl group having from about 1 to about 20 carbon atoms, an alkoxy group having from about 1 to about 12 carbon atoms, a substituted or unsubstituted aryl group containing from about 6 to about 12 carbon atoms, or NR''', wherein R''' is an alkyl containing from about 1

- 1 to about 12 carbon atoms; X is a halide; a is 0 or 1;
b is 0-4; c is 0-4; and the sum of a, b, and c is
equal to the oxidation state of M; and
(c) recovering said contact product of step
5 (b).

2. The supported metallocene catalyst of
Claim 1 wherein said acrylate has the formula:



- 10 wherein R is hydrogen or methyl and R¹ is an alkyl
group having from about 1 to about 12 carbon atoms or
an aryl group having from about 6 to about 12 carbon
atoms.

- 15 3. The supported metallocene catalyst of
Claim 2 wherein R is hydrogen and R¹ is a C₁₋₄ alkyl
group.

4. The supported metallocene catalyst of
Claim 3 wherein said acrylate is methyl acrylate.

- 20 5. The supported metallocene catalyst of
any one of Claims 1-4 wherein said particles range in
size from about 1 to about 1000 microns and the olefin
copolymer contains from about 70 to about 99 weight
percent C₂₋₄ α-olefin and from about 1 to about 30
25 weight percent of said acrylate.

6. The supported metallocene catalyst of
Claim 5 wherein said olefin copolymer contains from
about 80 to about 95 weight percent ethylene and from
about 5 to about 20 weight percent of said acrylate.

- 30 7. The supported metallocene catalyst of
any one of Claims 1-6 wherein said olefin copolymer is

1 selected from the group consisting of a copolymer of
ethylene-methyl acrylate, a copolymer of ethylene-
ethyl acrylate and a copolymer of ethylene-n-butyl
acrylate.

5 8. The supported metallocene catalyst of
Claim 7 wherein said olefin copolymer is ethylene-
methyl acrylate.

10 9. The supported metallocene catalyst of
any one of Claims 1-8 wherein said support is a
microfine powder comprised of particles which are
spherical or substantially spherical in shape and has
a median particle size ranging from about 1 to about
500 microns, from about 5 to about 300 microns, or
from about 20 to about 200 microns.

15 10. The supported metallocene catalyst of
any one of Claims 1-9 wherein said metallated compound
is a substituted or unsubstituted cyclopentadienylide,
indenylide or fluorenylide compound.

20 11. The supported metallocene catalyst of
Claim 10 wherein said metallated compound is a
compound selected from the group consisting of sodium
cyclopentadienylide, lithium cyclopentadienylide,
potassium cyclopentadienylide, lithium
pentamethylcyclopentadienylide, bis-(cyclopentadienyl)
25 magnesium, bis-(cyclopentadienyl) calcium,
cyclopentadienylthallium, sodium
pentamethylcyclopentadienylide, sodium indenylide,
lithium indenylide, sodium fluorenylide and lithium
fluorenylide.

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1 12. The supported metallocene catalyst of
any one of Claims 1-11 wherein from about 0.001 to
about 10 mmol metallated compound per gram particulate
olefin copolymer support is employed in step (a).

5 13. The supported metallocene catalyst of
any one of Claims 1-12 wherein steps (a) and (b) are
carried out in an inert atmosphere in the presence of
an ether solvent or an aromatic solvent.

10 14. The supported metallocene catalyst of
Claim 13 wherein said inert atmosphere is a N₂ or an
Ar gas atmosphere.

15 15. The supported metallocene catalyst of
Claim 13 wherein said ether solvent is selected from
the group consisting of tetrahydrofuran, dimethyl
ether, diethyl ether, di-n-propyl ether, diisopropyl
ether, di-n-butyl ether, divinyl ether, diallyl ether,
diphenyl ether, dimethoxyethane and 1,4 dioxane.

20 16. The supported metallocene catalyst of
any one of Claims 1-15 wherein step (a) is conducted
at a temperature of from about 0°C to about 100°C for
a period of time of about 1 hr to about 5 days.

25 17. The supported metallocene catalyst of
any one of Claims 1-16 wherein said intermediate of
step (a) may optionally be washed and dried prior to
performing step (b).

30 18. The supported metallocene catalyst of
any one of Claims 1-12 wherein said transition metal
compound is selected from the group consisting of
titanium trichloride, titanium tetrachloride,
zirconium tetrachloride, hafnium tetrachloride,
(cyclopentadienyl)titanium trichloride,

- 1 (cyclopentadienyl) zirconium trichloride,
(cyclopentadienyl) hafnium trichloride, zirconium
tetramethyl, zirconium tetramethoxy, zirconium
tetraethoxy, titanium tetramethyl, titanium
5 tetramethoxy, titanium tetraethoxy,
(cyclopentadienyl) zirconium tribromide,
(cyclopentadienyl) zirconium trimethyl,
(cyclopentadienyl) zirconium triphenyl, zirconium
tetra((dimethyl)amide), zirconium
10 tetra((diethyl)amide), cyclopentadienyl zirconium
dimethylamide dichloride and
(cyclopentadienyl) zirconium trimethoxy.

19. The supported metallocene catalyst of
any one of Claims 1-18 wherein step (b) is conducted at
15 a temperature of from about 0°C to about 100°C for a
period of time up to about 5 days.

20. The supported metallocene catalyst of
any one of Claims 1-19 wherein said supported
metallocene contains from about 0.01 up to about 10
20 weight percent of said transition metal, based on the
total weight of said catalyst.

21. An alpha-olefin polymerization catalyst
system comprising the supported metallocene catalyst
obtained in any one of Claims 1-20 and at least one
25 cocatalyst compound containing a metal from Groups IA,
IIA, IIB, IIIB or IVB of the Periodic Table of
Elements.

22. The alpha-olefin polymerization
catalyst system of Claim 21 wherein said cocatalyst is
30 a metal alkyl, metal hydride, metal alkylhydride or
metal alkylhalide.

1 23. The alpha-olefin polymerization
catalyst system of Claim 22 wherein the cocatalyst is
a cyclic or linear aluminoxane.

5 24. The alpha-olefin polymerization
catalyst system of Claim 23 wherein the cocatalyst is
methylaluminoxane.

10 25. The alpha-olefin polymerization
catalyst system of any one of Claims 21-24 wherein the
cocatalyst is added in a molar ratio of about 1:1 to
about 10,000:1 based on the transition metal compound
of said catalyst.

 26. The alpha-olefin polymerization
catalyst system of any one of Claims 21-25 further
comprising a cocatalyst modifier.

15 27. The alpha-olefin polymerization
catalyst system of Claim 26 wherein the cocatalyst
modifier is a halosilane, a halocarbon, an aromatic
ester, an organometallic compound, an alkoxysilane or
a phenylborate salt.

20 28. The alpha-olefin polymerization
catalyst system of Claim 27 wherein the phenyl borate
salt is triethylammonium tetraphenylborate, tri(n-
butyl)ammonium tetraphenylborate, trimethylammonium
tetraphenylborate, dimethyldiphenylammonium
25 tetraphenylborate, methylpyridinium tetraphenylborate,
benzylpyridinium tetraphenylborate, trimethylsulfonium
tetraphenylborate, triethylammonium
tetrakis(pentafluorophenyl) borate, triphenylammonium
tetrakis(pentafluorophenyl) borate,
30 methyldiphenylammonium tetrakis(pentafluorophenyl)
borate, anilinium tetrakis(pentafluorophenyl) borate,

1. methylanilinium tetrakis(pentafluorophenyl) borate,
dimethyl(m-nitroanilinium tetrakis(pentafluorophenyl)
borate, pyridinium tetrakis(pentafluorophenyl) borate,
N-methylpyridinium tetrakis(pentafluorophenyl) borate,
5 trimethylsulfonium tetrakis(pentafluorophenyl) borate,
tetraphenylphosphonium tetrakis(pentafluorophenyl)
borate, triphenylphosphonium
tetrakis(pentafluorophenyl) borate and
hexafluoroarsenic acid triethylammonium.
- 10 29. A process for (co)-polymerizing α -
olefins comprising polymerizing at least one C_2-C_8 α -
olefin under polymerization conditions in the presence
of the polymerization catalyst system of any one of
Claims 21-28, wherein the cocatalyst is added in a
15 molar ratio of about 1:1 to
about 10,000:1 based on the transition metal compound
of said catalyst.
- 20 30. The process of Claim 29, wherein said
 α -olefin is (co)polymerized into a polymer or
copolymer having substantially spherical particles
whose median particle sizes range from about 10 to
about 5000 microns.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/06447

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C08F 4/02, 4/60

US CL : 502/109, 127

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/109, 127

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5,492,985 A (PEIFER ET AL) 20 February 1996.	1-6
Y	US 3,422,049 A (MCCLAIN) 14 January 1969, entire document.	1-6
Y	EP 0,522,581 A1 (IDEMITSU KOSAN COMPANY LIMITED) 13 January 1993, entire document.	1-6
Y	JP 6-56928 A (UBE INDUSTRIES, LTD.) 01 March 1994, see translation page 12.	1-6

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

12 JUNE 1996

Date of mailing of the international search report

11 JUL 1996

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

 Authorized officer *C. T. S. J. f. w.*
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Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/06447

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 7-30
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.